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INVITED PAPER

A STUDY OF VIBRATIONAL AND LIBRATIONAL DYNAMICS IN MOLECULAR CRYSTALS BY PICOSECOND CARS

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Optical relaxation and dephasing of excitons, vibrons and librons has been a subject of continuing interest in the past decade. Photon echo and free induction decay experiments on optical excitons so far have not been reported, mainly I suppose because of experimental problems. With the currently available ps dye-lasers it should be possible however to obtain ps grating echoes [1] from the first singlet state in pure naphthalene. It has recently become clear that another coherent technique, coherent anti-Stokes Raman scattering (CARS) might be more appropriate to study collective excitations in solids. The third-order susceptibility $\chi^{(3)}$ which determines the macroscopic polarization that generates the coherent Raman signal may to a good approximation be written as:

$$\chi^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \chi^{(3)}_{NR} + \sum_v \frac{A_v}{\omega_v - (\omega_1 - \omega_2) + i\Gamma_v} + \sum_t \frac{A_t}{\omega_t - 2\omega_1 + i\Gamma_t} \qquad (1)$$

where ω_v the vibrational frequency is near $(\omega_1-\omega_2)$, ω_t the frequency of a two-photon resonance; Γ_v and Γ_t dephasing rate constants and A_v and A_t parameters proportional to the cross-sections for each process. There are two ways that CARS can be generated: a) in a continuous fashion, whereby from the *dispersion* of the CARS signal near a vibrational or electronic (two-photon) resonance the damping parameters are obtained. This technique has recently successfully been applied to molecular crystals [2,3]. b) in a time-resolved CARS experiment where a delayed pulse probes the remaining coherence in the sample. This technique has been developed and used by Laubereau and Kaiser [4] to study vibrational dephasing in liquids. Recently in our lab. we have employed ps delayed CARS to study both vibrational [5] and librational [6] relaxation in solid naphthalene. We are presently involved with a ps delayed CARS experiment on the lowest electronically excited g-state in biphenyl.

The basic problem with the CARS technique is that, in principle, the total inhomogeneously broadened lineshape is exposed. Fortunately enough it was shown [3,5,6] that the lineshapes of the vibron and libron excitations in naphthalene at 1.5K seem perfectly Lorentzian which suggests that the inhomogeneous broadening in these transitions is averaged out. Whether this effect also occurs in weak electronic transitions (like biphenyl) remains to be seen.
From the temperature dependence of the libron relaxation in naphthalene it is concluded that phase-matched decay is induced by cubic phonon anharmonicity.
We have recently noted in a delayed ps CARS study of naphthalene that, under certain excitation conditions, apparently there is strong interference between the generation of coherent Brillouin and Raman scattering. Detailed understanding of this effect is presently lacking. It is very clear however [7] that four-wave mixing spectroscopy is rapidly becoming an extremely useful and viable tool for spectroscopic applications.

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